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Mesomorphism Dependence on Terminally Substituted End Group

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A novel homologous series of liquid crystalline substances has been synthesized and studied with a view to understanding and establishing the relation between liquid crystal properties and molecular structure. The novel ester series consists of eleven enantiotropically smectogenic homologous without exhibition of nematogenic property. Transition temperatures were determined with an optical polarizing microscope equipped with a heating stage. Textures of smectic mesophase are focal conic fan shaped of smectic A or C type. Analytical and spectral data confirms the molecular structures of homologous. Transition curve, Cr-Sm behaved in normal manner. Transition curve Sm-I behaved in a normal manner up to the octyloxy (C_8) homolog derivative and then behaved in the unusual manner for the C_{10}, C_{12}, C_{14}, and C_{16} derivatives. An odd-even effect is observed for the Sm-I transition curve. The series entirely smectogenic with a middle-ordered melting type and a moderate mesophase length. The average thermal stability for smectic is 128.09°C and mesophase length ranges from 8.6°C to 73.2°C. The mesomorphic (LC) behavior of the novel series is compared with structurally similar known homologous series.

Keywords Enantiotropy; lamellar packing; liquid crystals; mesomorphic; smectic

Introduction

In 1888 [1], the liquid crystal (LC) state was recognized as a separate state of matter intermediate to the crystalline solid state and the isotropic liquid state. Since that time many LC substances have been reported [2–6] by chemists and other scientific researchers. LC substances due to their unique applications have attracted research groups of all branches of science and technology [7–9]. LC materials vary massively with different shape, size, aromaticity, positions of functional group or groups, moieties, molecular polarities, and polarizabilities of different magnitudes of rigidity and flexibilities, responsible to induce LC state requires [10–13]. Therefore, the present investigation is planned with a view to understanding and establishing the correlation between the LC state and molecular structures [14–16] by synthesizing novel LC substances with three phenyl rings bonded through −CH=CH−COO− and −COO−CH_2- Central bridges; –OR and −Cl terminal end groups which may induce mesophase formation and prove their ability and usefulness in applications. The present investigation will include synthesis, characterization, and discussion

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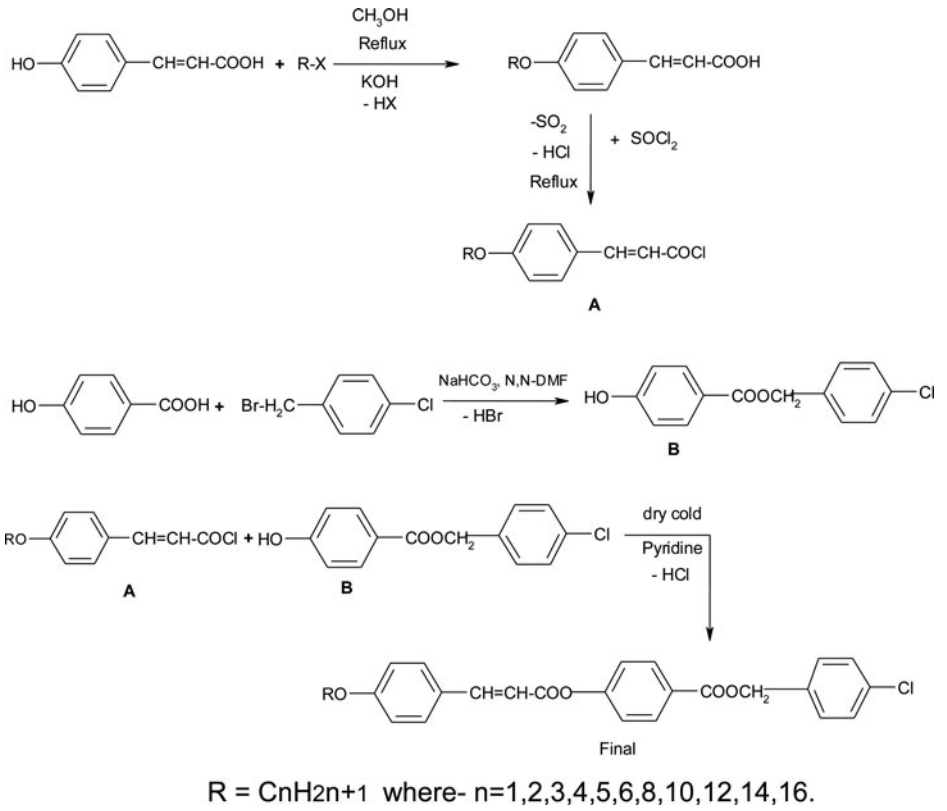
about the relation between LC states, as well as some LC properties and molecular structure.

Experimental

Synthesis

4-Hydroxy cinnamic acid was alkylated by suitable alkylating agent R-X to form *n*-alkoxy cinnamic acids by a modified method of Dave and Vora [17]. 4-Hydroxy-4′-chlorobenzyl benzoate (m.p:120°C–130°C) was prepared from 4-chloro benzyl bromide and 4-hydroxy benzoic acid by applying the method of a US patent No.0053964 and European patent and the modified method of Doshi and Patel [18]. *n*-Alkoxy cinnamic acids, through their corresponding acid chlorides, and 4-hydroxy-4′-chlorobenzyl benzoate were condensed in dry pyridine to form final products by an established method [19]. The final esterified products were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures were obtained.

4-Hydroxy cinnamic acid, alkyl halides, methanol, KOH, 4-chloro benzyl bromide, *N,N*-dimethyl formamide, $NaHCO_3$, HCl, dry pyridine, thionyl chloride, EtOH, etc. required for the synthesis were used as received, except for solvents which were dried and purified prior to synthesis. The synthetic route to the series is shown below in scheme-1.



Scheme 1. Synthetic route to the series.

Characterization

The characterization of some selected members of a novel homologous were analyzed by elemental analysis (Table 1), structure elucidation by infrared spectra, ^{1}HNMR spectra, mass spectra. Textures, and Transition temperatures of homologous, as well as of related materials were determined by an optical polarizing microscope, equipped with a heating stage. Elemental analysis was performed on Perkin-Elemer PE 2400 C,H,N analyzer. IR spectra were recorded on Perkin-Elemer GX spectrometer. ^{1}HNMR spectra were determined on a Bruker spectrometer using $CDCl_3$ solvent. The textures of the smectic mesophase of some homologous were recognized either directly from the microscopic observations or by a miscibility method.

Analytical Data

Spectral Data

^{1}HNMR in ppm for the dodecyloxy derivative: 1.21 ($-CH_3$ of $C_{12}H_{25}$), 3.92 ($-CH_2$- of $-C_{12}H_{25}$), 5.23–5.30 ($-CH{=}CH-$), 6.25–6.29 (p-substituted phenyl ring), 7.82–7.84 (p-substituted benzene).

^{1}HNMR in ppm for the decyloxy derivative: 0.85 ($-CH_3$ of $C_{10}H_{21}$), 1.23 ($-CH_2$- of $-C_{10}H_{21}$), 3.93 ($-O-CH_2$-), 5.23–5.30 ($-CH{=}CH-$), 6.24–6.29 (p-substituted phenyl ring), 6.53–6.57 (p-substituted benzene).

NMR Data Confirm the Structure

IR in cm^{-1} for octyloxy derivative: 722 polymethylene of C_8H_{17}, 830 para-substituted phenyl ring, 1092, 1115, 1673 ester linkage of ($COO-C_8H_{16}$), 982 Trans of ($-CH{=}CH-$) 1166, ether linkage of (C_8H_{17}-O$-$ of phenyl), 1016 Aromatic $-$Cl linkage.

IR in cm^{-1} for hexadecyloxy derivative: 720 poly methylene of $C_{16}H_{33}$, 829 para substituted benzene, 981 Trans ($-CH{=}CH-$), 1017 Aromatic $-$Cl linkage, 1105, 1243, 1672 ($-COO-$), 1166 ether linkage of ($C_{16}H_{33}-O-C_6H_4$), 3399 (H$-$ bonding of OH).

IR Data Confirm the Structure

Mass Spectra. Mass spectra for hexyloxy derivative:

Molecular weight: Calculated: 493. Molecular formula: $C_{29}H_{29}ClO_5$

Experimental: 496.

Texture of Smectic phase by miscibility method

Butyloxy (C_4) derivative ——————→ Smectic – A

Octyloxy (C_8) derivative ——————→ Smectic – A

Tetradecyloxy (C_{14}) derivative————→ Smectic – C

Hexadecyloxy (C_{16}) derivative ————→Smectic – C

Results and Discussion

4-*n*-Alkoxy cinnamic acids on condensation with 4-hydroxy-(4′-chloro benzyl) benzoate yielded novel ester derivatives of LC property. All the members of the series (C_1–C_{16}) are enantiotropic smectic without exhibition of nematogenic mesomorphism. Transition temperatures as recorded in Table 2 were plotted versus the number of carbon atoms

Table 1. Elemental analysis for methyloxy, ethyloxy, propyloxy, and butyloxy derivatives

		% Elements calculated (experimental%)		
Sr. no.	Molecular formula	C	H	Cl
1	$C_{24}H_{19}ClO_5$	66.16(63.22)	4.50(4.78)	8.40(7.94)
2	$C_{25}H_{21}ClO_5$	68.72(66.88)	4.81(4.63)	8.13(8.44)
3	$C_{26}H_{23}ClO_5$	69.25(70.20)	5.10(4.80)	7.88(8.10)
4	$C_{27}H_{25}ClO_5$	69.75(68.30)	5.38(5.00)	7.64(7.10)

present in the *n*-alkoxy terminal end group. Like or related points were linked to draw a phase diagram consisting of Cr-Sm and Sm-I transition curves showing the phase behavior of a novel series. The Cr-Sm transition curve majorly adopts a zigzag path of rising and falling values and behaves in normal manner. The Sm-I transition curves for odd and even members of the series initially rise and then descend up to the octyloxy (C_8) homolog in a normal manner, but then beyond the octyloxy homolog it deviates for the decyloxy (C_{10}), dodecyloxy (C_{12}), and tetradecyloxy (C_{14}) derivatives, to which the Sm-I transition temperatures rise instead of fall as compared to the octyloxy (C_8) derivative. Thus, the Sm-I transition curve adopts a serpantile shape. The transition curves for the odd and even homologous merge into each other at the heptyloxy (C_7) homolog and for higher homologous continue as a single Sm-I transition curve. The average thermal stability for smectic is *128.09°C* and the degree of smectogenic mesomorphism varies from 8.6°C to 73.2°C. The mesomorphic property of the novel series varies from homolog to homolog depending upon the varying length of the *n*-alkoxy terminal end group.

Linking of the *n*-alkoxy cinnamic acids, through their corresponding acid chlorides, with 4-hydroxy-(4′-chlorobenzyl) benzoate (m.p: 120°C–130°C), increases the molecular length and length to breadth ratio, dipole moment across the long molecular axis,

Table 2. Transition temperatures of series in °C

		Transition temperature in C		
Compound no.	$R = C_nH_{2n+1}(n)$	*Sm*	*Nm*	Isotropic
1	C_1	86.0	—	95.8
2	C_2	104.4	—	121.6
3	C_3	102.9	—	134.0
4	C_4	100.2	—	135.8
5	C_5	98.0	—	118.7
6	C_6	109.1	—	126.9
7	C_8	113.4	—	122.0
8	C_{10}	118.2	—	151.1
9	C_{12}	114.5	—	131.9
10	C_{14}	84.6	—	157.8
11	C_{16}	89.8	—	113.4
Sm: Smectic	*Nm:* Nematic			

dipole–dipole interactions, dispersion forces, etc. Suitable magnitudes of anisotropic forces of intermolecular attractions as a consequence of favorable molecular rigidity and flexibility induce smectogenic character. The molecules of the novel homologous of the ester series (C_1–C_{16}) show a high resistivity toward externally exposed thermal vibrations and disaligned at an angle ninety degree or less than ninety degrees. All the homologous of the present novel series possess lamellar packing of the molecules in their layered lattices, which under the influence of exposed thermal vibrations, acquire a focal conic molecular networking and sliding layered arrangement of molecules for definite range of temperatures to induce a smectic mesophase of the type A or C. However, smectogenic molecular arrangement ceases to appear at the respective isotropic temperatures without passing through less ordered molecular arrangement of the nematic phase. The smectogenic mesophase reappears reversibly on cooling the melt from and below isotropic temperatures in reversible manner. The exhibition of an odd-even effect in the Sm-I transition curve is attributed to the odd- and even-numbered methylene units present in the *n*-alkoxy terminal end group. Ceasing of appearing odd-even effect from and beyond the C_7 homolog is due to the *n*-alkyl chain, which may coil, bend, flex, or couple to lie with major axis of the core structure of a molecule. Variations in LC behavior from homolog to homolog in the novel series is due to the sequentially and progressively added methylene unit which alters the suitable magnitudes of anisotropic forces of intermolecular attractions as a consequence of changing molecular rigidity and flexibility. The deviating trend in LC behavior of the higher homologous may be attributed to the uncertainty arising from the status of *n*-alkyl chain or its effective chain length, which is related to dipole–dipole interactions across the long molecular axis as a result of net intermolecular cohesive energy and closeness. Thus suitable magnitudes of anisotropic forces of intermolecular attractions facilitated and stabilized lamellar molecular packing in crystal lattices to cause smectic mesophase formation.

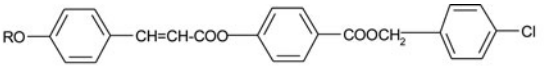
The mesogenic properties of presently investigated novel homologous series-1 are compared with the structurally similar homologous series-X [20] as shown in Fig. 1.

Homologous series-1 of present investigation and a structurally similar homologous series-X chosen for comparative study are identical in every way except for the presence or absence of the terminal chloro substituent, as seen in Fig. 1. Thus, the magnitudes of the combined effects of molecular rigidity and flexibility governing the tendency of a substance to induce or facilitate and stabilize LC properties, which vary from homolog to homolog in the same series it also vary for the same homolog from series to series. Therefore, the mesomorphic (LC) property and the degree of mesomorphism are depended upon the suitable magnitudes of anisotropic forces of intermolecular attractions as a consequence of individual molecular rigidity and flexibility as emerged due to dipole–dipole interactions, permanent dipole moment of molecule, dispersion forces, intermolecular closeness, etc. which vary with molecular structure and induce variations in mesomorphic behaviors of every substance. Table 3 shows some LC properties, such as thermal stability, commencement of LC phase, type of mesophase, and the mesophase length range, etc. for the present novel series-1 and series-X chosen for comparison.

From the Table 3, it is clear that,

Homologous novel series-1 is only smectogenic, whereas series-X is only nematogenic. Thus, series-1 missing nematogenic property and series-X is missing smectogenic property.

Mesophase formation comencences from very first member (C_1) of a novel series-1 and it commences late from the sixth member (C_6) of series-X.



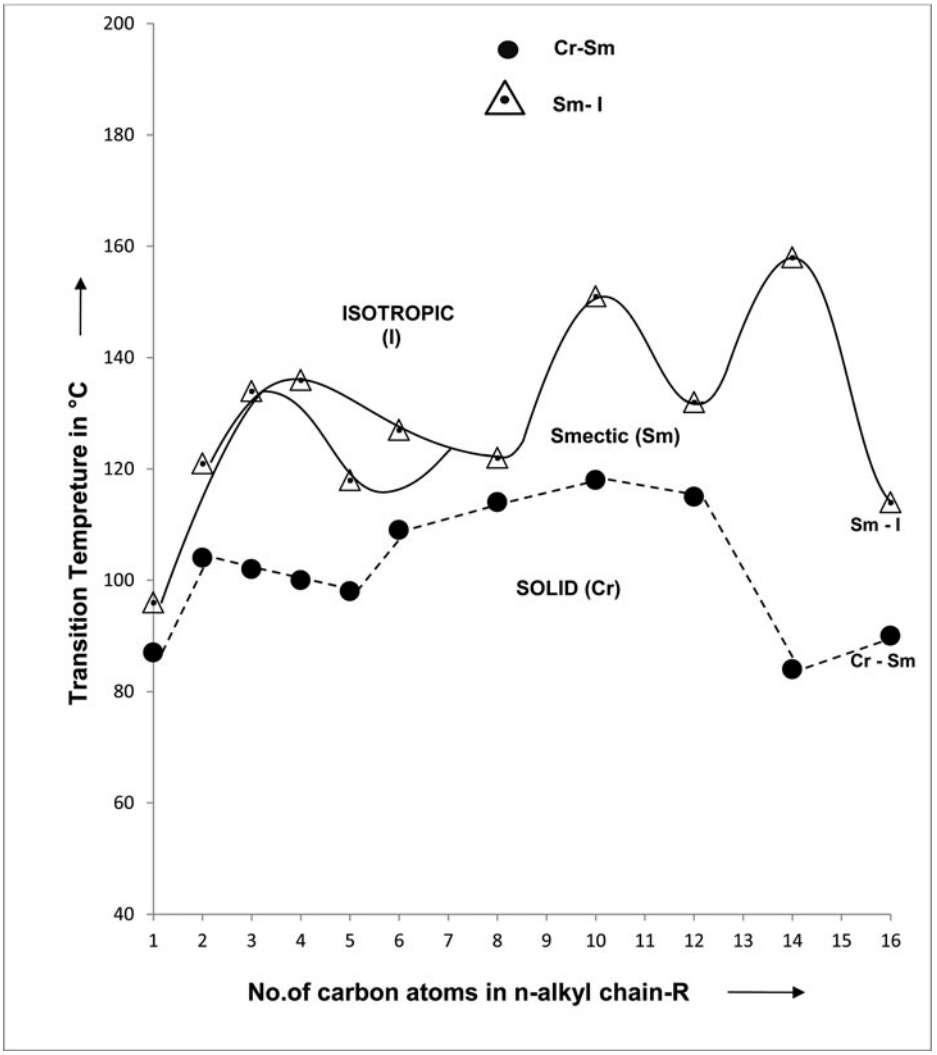


Figure 1. Phase behavior of series.

Table 3. Average thermal stability in °C

Series→	1	X
Smectic–isotropic or smectic—nematic	128.09 (C_1–C_{16})	—
Commencement of nematic phase	C_1	—
Nematic–isotropic	—	153.1 (C_6–C_{16})
Commencement of nematic phase	—	C_6
Mesophaselength range in °C	Sm 8.6 to 73.2	Nm 12 to 50

Mesomorphic phase length ranges from 8.6°C to 73.2°C for series-1 (Sm), whereas same is ranging from 12°C to 50°C (*N*) for series-X.

Average thermal stability of LC phase (Sm) is 128.09 of series-1, whereas it is higher than series-X 153.1 (*N*).

C_1 to C_{16} members of a series-1 are mesomorphic (Sm), whereas less number (C_6–C_{16}) of members of series-X are mesomorphic (*N*).

Terminal –H of series-X is weakly polar and relatively possess zero inductive effect than equally situated −Cl terminal end group, because the electron accepting tendency or electronegativity of –H is lower than −Cl. Therefore, the bond polarities of C−H is poorer than that of C−Cl. Thus, the vector sum (not algebraic sum) of all the bonds in a molecule related to series-1 and X, the magnitudes of permanent dipole moment, dipole–dipole interactions, electronic interactions, dispersion forces, etc. are relatively lower for a series-X as compared to series-1. Therefore, intermolecular cohesion energy and closeness for the same homolog from series to series related to suitable magnitudes to anisotropic force to induce LC behaviors, either as smectic or nematic mesophase formation for the present series-1 is higher (or for the series-X is lower than series-1) than a series-X. Hence, the suitable magnitudes of LC phase formation is missed by methoxy to pentyloxy (C_1–C_5) homologous of series-X i.e., late commencement of less ordered mesophase formation (*N*) is facilitated and stabilized in case of series-X. However, under identical situation in case of series-1, the suitable magnitudes of anisotropic forces of intermolecular cohesion commences from a very first member to last member of a series facilitating and stabilizing higher ordered mesophase (smectic) formation. The Sm-I transition temperatures of series-1 are relatively lower than the N-I transition temperature which gives average thermal stability lower for smectic of a series-1 and higher for nematic of series-X. Also, it is normally observed for any same homologous series that N-I transition temperatures are higher than the Sm-I transition temperatures. The resistivity toward externally exposed thermal vibrations of the molecules of present series-1 due to higher intermolecular cohesive energy facilitated and stabilized three dimensional net working of molecules in their crystal lattices to exhibit smectogenic mesophaselength worth from 8.6°C to 73.12°C, while it is 12–50°C which is lower for series-X. Thus variations in LC properties and the degree of mesomorphism are depended upon the degree variations of molecular structures.

Conclusions

Presently investigated chloro-substituted (para) homologous series is entirely smectogenic without exhibition of any nematogenic character.

Group efficiency order derived for smectic and nematic on the basis of (i) thermal stability (ii) early commencement of mesophase, and (iii) mesophaselength is as under

Smectic: −Cl > −H
Nematic: −H > −Cl
Smectic: −Cl > −H
Nematic: −H > −Cl
Smectic: −Cl > −H
Nematic: −H > −Cl

Mesophase formation and the LC properties are very sensitive and susceptible to the molecular structure.

Molecular rigidity and flexibilities of suitable magnitudes as a consequence of molecular structure are the basis of LC phase formation.

The variations in LC behaviors from homolog to homolog in the same series is due the changing number of methylene units in *n*-alkoxy terminal end group keeping right handed terminal end group unchanged.

The variations in LC properties for same homolog (same –OR group) from series to series are due to the variations of right-handed terminal end group.

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